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SERS monitoring of the catalytic reduction of 4-nitrophenol on Ag-doped titania nanoparticles

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ABSTRACT

Nitrophenols represent common environmental pollutants because of their toxicity and resistance to microbial degradation. In the present work the SERS (surface-enhanced Raman scattering) spectroscopy has been applied to Ag/titania colloidal nanocomposites to monitor the catalytic reduction of 4-nitrophenol under UV irradiation and identify the reaction products.

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1. Introduction

Materials made up of grains or clusters in the nanometer range exhibit peculiar optical, chemical and magnetic properties of interest in many application areas of the materials science, such as the fabrication of electroluminescent devices and nanosensors. For example, thin films of titania, formed of nanosized particles in the anatase form [1,2], show very high photocatalytic efficiency by means of UV irradiation. In this way it is possible that the degradation of pollution agents occurs in the presence of nanostructured titania surfaces [3–5]. The Raman spectroscopy allows identifying products of photocatalytic reactions by observing the vibrational spectra. However, a severe limitation to the use of this spectroscopic technique relies on the scarce sensibility ensured by Raman scattering measurements. This problem can be satisfactorily overcome by the enhancement of the Raman signal of adsorbed reagents or products, due to the presence of nanosized particles of metals like silver, gold or copper. This enhancement can reach values of several orders of magnitude in the so-called SERS (surface-enhanced Raman scattering) spectroscopy [6,7]. Hence, the aim of this project is to combine the catalyzing properties of titania and the spectroscopic ones of SERS-active metals, by doping colloidal titania with silver nanoclusters. Hence, the SERS spectroscopy allows studying the photocatalytic reactions occurring at the Ag/titania surface, by observing the spectroscopic changes after UV irradiation and recognizing the adsorbed reaction products. An important class of pollutants, arousing apprehension for their toxicity and mutagenicity, is constituted by aromatic nitroderivatives, in particular nitrophenols, which are responsible of serious damages for vegetation [8]. Actually, the degradation of nitrophenols represents a big challenge for the environmental chemistry [9,10]. In the present work Ag-doped colloidal titania substrates have been prepared for monitoring by SERS spectroscopy the photodegradation of 4-nitrophenol that rapidly soaks the soil, where it is accumulated with devastating effects for the environment.

2. Experimental

Silver colloids (pH ~9) were prepared following the Creighton's procedure [11], by adding silver nitrate (Aldrich, purity 99.998%) to an aqueous solution of excess sodium borohydride (Aldrich, purity 99%) as reducing agent. The same procedure was followed for obtaining Ag/titania colloids by reduction of silver ions in the presence of colloidal titania (0.001 wt%), provided by Aldrich. In the SERS measurements, week-aged colloids were used to prevent formation of reduction products due to the presence of residual borohydride [12]. In order to obtain a SERS-activation of both pure Ag and Ag-doped titania colloids, NaCl (Aldrich, purity 99.999%) was added in small amounts (~10^{-3} M). The addition of chloride anions provides also a suitable colloidal stabilization.

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4-Nitrophenol (Aldrich, purity) was added (10^{-4} M concentration) to the aqueous colloidal suspensions of both pure Ag and Ag-doped titania.

The quartz cell containing 4-nitrophenol in pure Ag or Ag-doped titania hydrosol was exposed to a UV lamp (Mineralight, UVS-11) with peak emission at 254 nm. The lamp was kept at a distance of 10 cm from the cell.

UV–vis absorption spectra of colloidal titania, silver hydrosol and Ag-coated colloidal titania were obtained in the 200–800 nm region by using a Cary 5 Varian spectrophotometer.

Raman spectra were recorded using the 514.5-nm line of a Coherent Argon ion laser, a Jobin-Yvon HG2S monochromator equipped with a cooled RCA-C31034A photomultiplier and a data acquisition facility. To reduce the thermal effects due to the laser light, a defocused beam with low power (20 mW) was used for irradiating the colloidal samples. Power density measurements were performed with a power meter instrument (model 362; Scientech, Boulder, CO, USA) giving ~5% accuracy in the 300–1000 nm spectral range.

Infrared spectra of 4-nitrophenol in KBr pellet were obtained in the 4000–450 cm^{-1} region by using a PerkinElmer FT-IR RX/I spectrometer.

Transmission electron microscopy (TEM) measurements on Ag/titania hydrosols were obtained by using a Philips EM 201 instrument with an electron beam emitted at 80 kV, after placing a drop of colloidal sample on a carbon–Cu grid.

3. Results

As shown in Fig. 1 4-nitrophenol and its anion present two resonance forms, benzenoid and quinonoid, where a negative charge is located on the electron-withdrawing nitrogroup. By observing the Raman spectrum of 4-nitrophenol in water solutions at different pH values (Fig. 2a and b), marked intensity changes occur in alkaline medium for several bands, due to the deprotonation of the hydroxyl group. The quinonoid form of the anion is related to a large polarizability change, determining strong intensity variations in the Raman bands. The intensity of the band observed around 1340 cm^{-1}, assigned to the symmetric stretching mode of the nitrogroup [13], markedly decreases in alkaline aqueous solution, whereas the band at 1290 cm^{-1}, attributable to a ring deformation mode mixed with the nitrogroup stretching mode, becomes quite intense. The most intense band at alkaline pH, however, is observed around 860 cm^{-1}, attributable to the nitrogroup bending mode mixed with CC stretching mode.

In Ag hydrosol a SERS spectrum is observed (Fig. 2c), which appears quite similar to the Raman spectrum in alkaline medium (Fig. 2b), where 4-nitrophenolate is largely predominant. This indicates that the molecule adsorbs on silver in the anionic form, probably through the hydroxyl oxygen, as previously suggested on

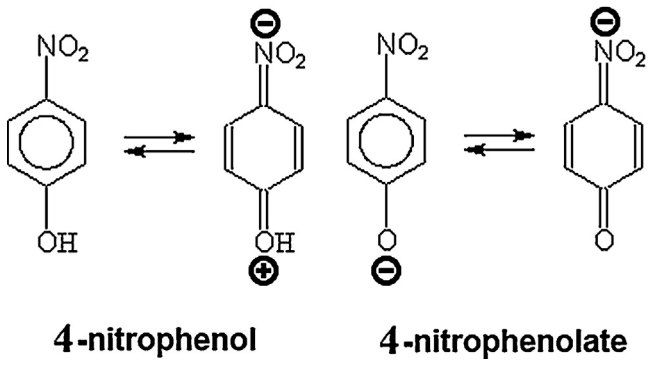

Fig. 1. Resonance structures of 4-nitrophenol and 4-nitrophenolate.

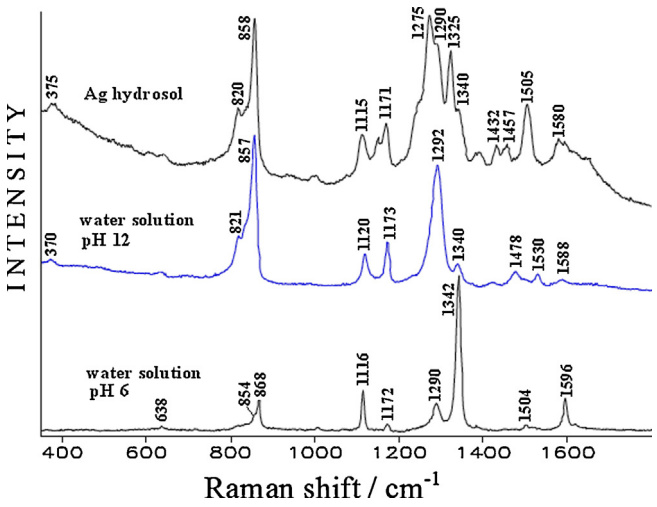

Fig. 2. Raman spectra of 4-nitrophenol in water at different pH values, compared with the SERS spectrum in Ag hydrosol.

the basis of SEIRA (surface-enhanced infrared absorption spectrometry) measurements [14]. However, the occurrence of some bands with medium intensity, for example those at 1325 and 1290 cm^{-1}, could be interpreted with a minority presence of adsorbed neutral molecules. In this case, the downshift of the nitrogroup stretching mode from 1342 cm^{-1} (Raman) to 1325 cm^{-1} (SERS) suggests that the adsorption could occur via nitrogroup.

As shown in the UV–vis absorption spectra (Fig. 3), the SPR (surface plasmon resonance) peak of the silver nanoparticles is red-shifted from 390 to 410 nm for Ag/titania colloidal suspensions. This indicates that silver adheres to the titania surface by forming large nanocomposites with mixed Ag/titania content. This is confirmed by TEM (transmission electron microscopy) measurements, as shown in Fig. 4. The images show silver clusters (size: 4–5 nm) adhering to titania particles (sizes: 50–100 nm), leaving a large part of the titania surface free to adsorb ligand molecules. No change is observed in the UV–vis absorption of the Ag-doped titania suspension, regarding both the plasmon resonance band and the spectral background, by addition of 4-nitrophenol and by UV-irradiation.

Different adsorptions could occur when the molecule interacts with pure Ag nanoparticle or with Ag/titania nanocomposite. Fig. 5

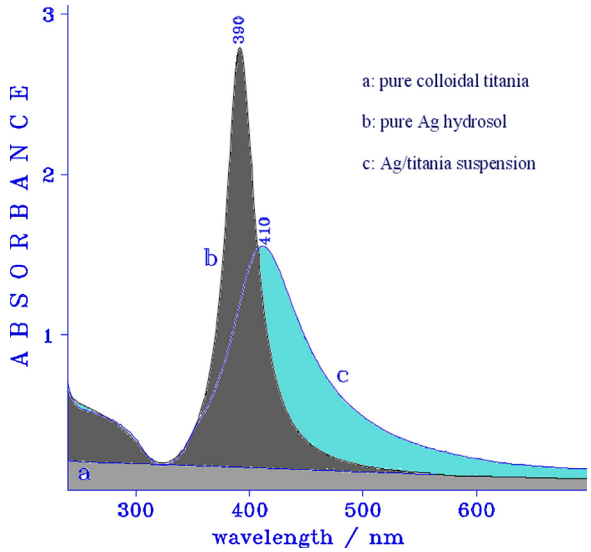

Fig. 3. UV–vis absorption spectra of aqueous colloidal suspensions containing pure titania particles (a), pure Ag particles (b) and Ag/titania particles (c).

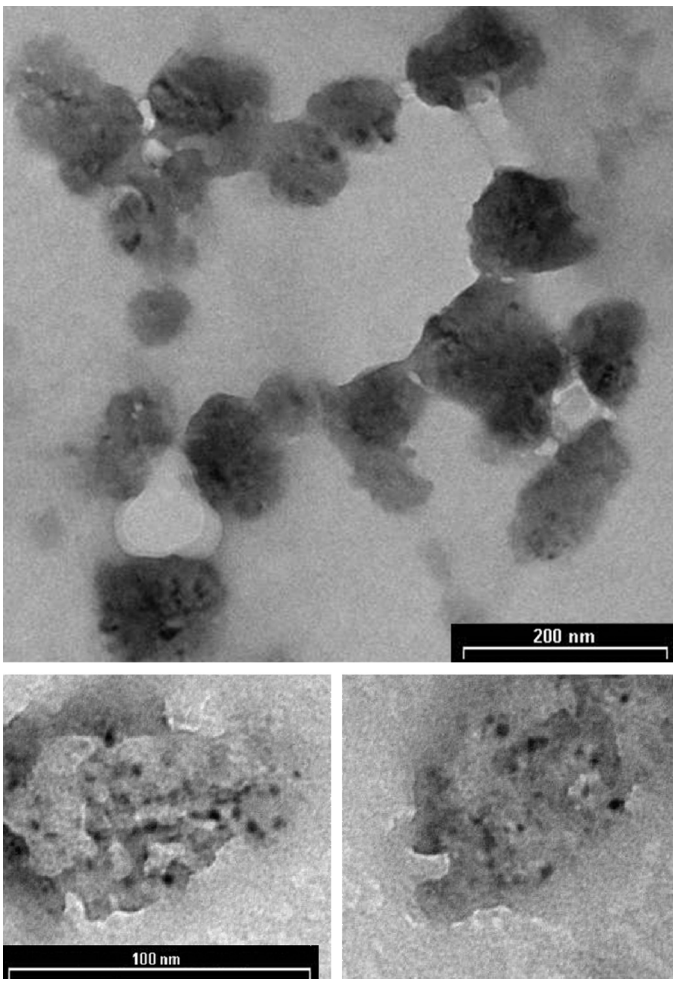

Fig. 4. TEM images of Ag/titania colloidal particles at different magnifications.

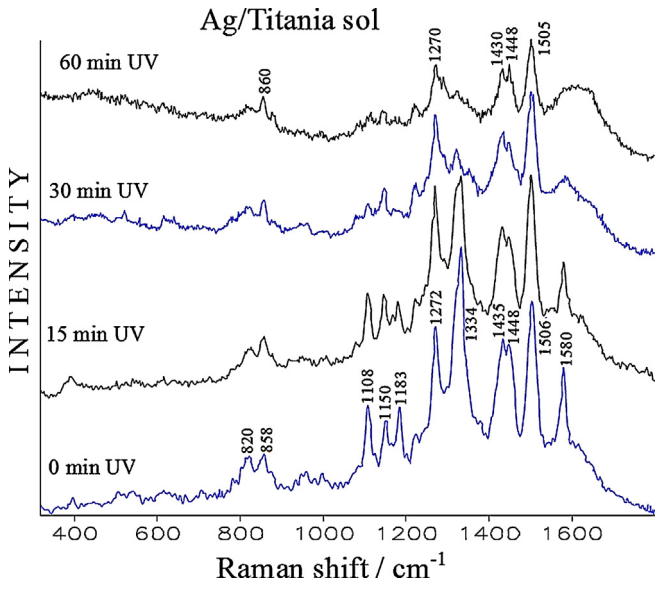

Fig. 5. SERS spectra of 4-nitrophenol in Ag/titania hydrosol after different UV irradiation times.

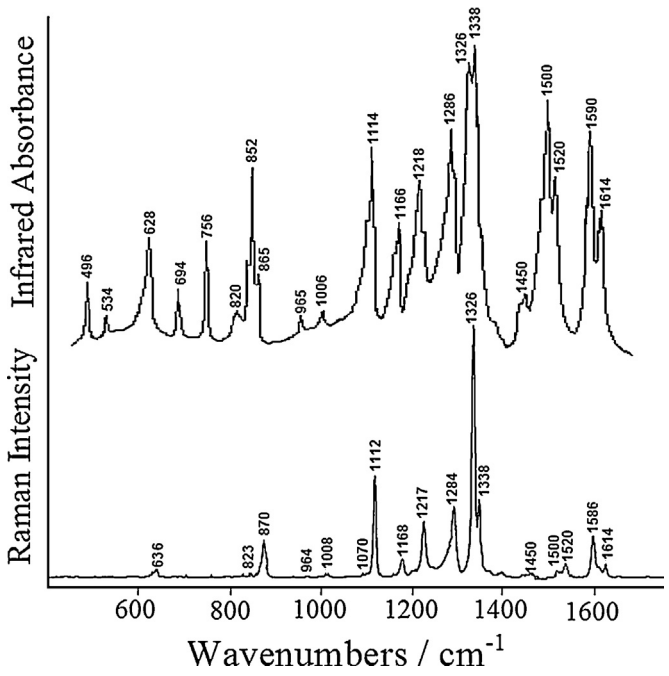

Fig. 6. Infrared and Raman spectra of solid 4-nitrophenol.

(lower trace) shows the SERS spectrum of 4-nitrophenol adsorbed on Ag-doped titania, resulting quite different from that observed in pure silver hydrosol (Fig. 2c). This fact suggests three important considerations: (a) the ligand adsorbs on the Ag-doped titania surface and not on pure Ag colloidal particles; (b) the doping of titania with silver clusters provides an efficient SERS enhancement; (c) the molecule/substrate interaction is different from that occurring on Ag hydrosol, where the presence of 4-nitrophenolate has been ascertained. Actually, the SERS on Ag/titania does not exhibit the spectroscopic features of the anion, shown in Fig. 2b and c. The most intense SERS band is observed at about 1330 cm^{-1}, attributable to the symmetric stretching mode of the nitrogroup, whereas weak bands occur below 1100 cm^{-1}, as well as for the normal Raman spectrum shown in Fig. 2a. Hence, one can assume that ligand is adsorbed as neutral molecule. The strongest SERS band, corresponding to the symmetric stretching mode of nitrogroup, is downshifted from 1342 cm^{-1} (Raman) to 1334 cm^{-1} (SERS), suggesting a chemical interaction with the substrate through this group. This adsorption is consistent with that proposed for 4-nitrophenol by DFT calculations [15] and analogously to other nitroarenes adsorbed on silver [16]. However, other intense SERS bands, which appear difficult to be assigned, occur in the range 1400–1600 cm^{-1}, in particular around 1440, 1500 and 1580 cm^{-1}. Actually, these bands can be related to vibrational modes of 4-nitrophenol, which appear quite strong in the infrared spectrum, as shown in Fig. 6 in comparison with the Raman spectrum of the solid sample. The observed vibrational bands of solid 4-nitrophenol are reported in Table 1, along with the assignment proposed on the basis of DFT calculations [15].

By UV-irradiation, however, the SERS spectrum undergoes significant changes, because the nitrogroup stretching band at about 1330 cm^{-1} progressively decreases in intensity up to disappearing, along with a marked lowering of the overall SERS enhancement, as shown in Fig. 5. This effect is not observed in pure Ag hydrosol after UV irradiation, because in this case the SERS bands do not undergo any modification in both positions and intensities. The spectral modifications occurring in Ag/titania colloid by UV irradiation can be related to the catalyzing action of the Ag/titania nanoparticles, which could provide by UV irradiation the electrons involved in

Table 1
Infrared and Raman bands of solid 4-nitrophenol.

Calculated[a] (cm^{-1})	Raman (cm^{-1})	Infrared (cm^{-1})	Assignment[a]
1597	1614	1614	Ring stretch
1585	1586	1590	Ring stretch
1528	1520	1520	NO_2 antisymm. stretch
1480	1500	1500	C—H ip bend
1424	1450	1450	C—H ip bend
1341	1338	1338	Ring stretch
1324	1326	1326	NO_2 symm. stretch
1288	1284	1286	C—H ip bend
1257	1217	1218	O—C stretch
1155	1172		C—H ip bend
1155		1166	O—H deform
1089	1112	1114	C—H ip bend
1085	1070		CCC bend
986	1008	1006	C—H ip bend
950	964	965	C—H op bend
934		960	C—H op bend
840	870	865	NO_2 bend
827	850	852	C—H op bend
789	823	820	C—H op bend
789	814	814	NO_2 bend
721	756	756	NO_2 op bend
653	694	694	C═O op bend
621	636		CCC bend
611	628	628	C═O bend
516	534	534	NO_2 ip bend
483	499	496	C═O op bend

[a] Ref. [15].

the reduction of the nitrogroup to aminogroup, according to the reaction:

$$R\text{-}NO_2 + 4H^+ + 6e^- \rightarrow R\text{-}NH_2 + 2OH^-$$

For this reaction the close vicinity of the nitrogroup to titania is necessary, confirming that the adsorption really occurs via nitrogroup. The photocatalytic reduction of 4-nitrophenol is analogous to those occurred to nitrobenzene when adsorbed on titania with silver nanoparticles [17,18].

The drastic decrease of the SERS enhancement after UV irradiation can be explained by considering that 4-aminophenol, produced by effect of the Ag/titania nanoparticles, does not strongly interact with the substrate, as, instead, occurs when the electron-drawing nitrogroup is present.

Finally, it is important to emphasize that Ag/titania nanocomposite exhibits high stability in time, in both absence and presence of ligand, as well as during the UV irradiation. This fact has been verified by monitoring the UV–vis absorption, along with the SERS spectra. Actually, the plasmon resonance band shown in Fig. 3, as well as the spectral background, does not undergo any change. This evidence points to the photocatalytic effect of the UV irradiation on the adsorbate, as evidenced by the SERS spectra, and not to possible modifications of the substrate.

4. Conclusions

We have prepared Ag-coated colloidal titania, which has been characterized by UV–vis absorption spectroscopy, TEM microscopy and Raman scattering. The Ag/titania nanoparticles are stable in aqueous dispersion and exhibit SERS efficiency, as shown for adsorbed 4-nitrophenol, whose Raman spectrum has been compared with that obtained in pure silver hydrosol. By UV irradiating the Ag/titania suspension the catalytic photoreduction of 4-nitrophenol occurs, which can be monitored by SERS measurements. The use of our colloidal nanocomposites could extend the SERS investigation to the photodegradation processes of other dangerous pollutants by effect of the catalytic activity of titania.

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